THE ESTERIFICATION OF ORTHO, META AND PARA TOLUIC ACIDS WITH ETHYL MERCAPTAN.

A DISSERTATION

Submitted to the Board of University Studies of Johns Hopkins University in Conformity with the Requirements for the Degree of Doctor of Philosophy.

By

JOHN HARRISON SACHS.

Baltimore, June 1916.

75253

THE ESTERIFICATION OF ORTHO, META AND PARA TOLUIC ACIDS WITH ETHYL MERCAPTAN.

A DISSERTATION

Submitted to the Board of University Studies of Johns Hopkins University in Conformity with the Requirements for the Degree of Doctor of Philosophy.

R. UNIV. BIBLIOTHEEK LEIDEN

By

JOHN HARRISON SACHS.

Baltimore, June 1916.

Gettysburg Compiler Print.
Gettysburg, Pa.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41547013_0026

TABLE OF CONTENTS

Acknowledgment 4
Historical 5
Materials 8
Heating 10
Procedure 11
Experimental 12
Results 14
Summary of Results 21
Discussion 22
Conclusion 24
Biography 25

ACKNOWLEDGMENT.

This investigation was carried out under the advice and assistance of Doctor Reid. I wish to take this opportunity to express to him my sincere appreciation of the help which he gave. I also feel under obligation to Drs. Remsen, Morse, Jones, Gilpin, Frazer, Lovelace, Swartz, and Acree for instruction and encouragement received from them.

THE ESTERIFICATION OF ORTHO, META AND PARA TOLUIC ACIDS WITH ETHYL MERCAPTAN.

HISTORICAL.

As early as 1862 Berthelot and Peau de St. Gilles[1] began the investigation of the general problem of esterification. They studied the limit of esterification for different temperatures. In 1878 Menschutkin[2] took up the problem and by using different alcohols with acetic acid first showed the effect of composition and isomerism in the rate and limit of esterification. Goldschmidt[3] in 1885 first studied the effect of differences of constitution in isomeric acids upon ester formation. He studied the esterification of ortho, meta and para substituted benzoic acids with ethyl alcohol, using HCl for a catalyzer. By using a large excess of alcohol in which was dissolved the HCl he was able to use for the calculation of his results the equation for a monomolecular reaction:

$$K = \frac{1}{t} \log \frac{a}{a - y}$$

For the toluic acids he got the following constants:

Ortho Toluic	0.011
Meta Toluic	0.0470
Para Toluic	0.0241

The same general relation was noted for other substituted benzoic acids.

1 Ann. Chem. et Phys. (3) 65, 385 (1862); 66, 5 (1862); 68, 225 (1863).
2 Menschutkin, A. 195, 334 (1878).
3 Goldschmidt, Ber. 18, 3218 (1895).

About the same time Petersen[4] observed that para toluic acid forms ester much more readily than does the ortho acid.

From 1894 to 1897 Victor Meyer[5] and his coworkers, investigating the problem of stearic hindrance, threw much light on the effect of isomers upon esterification. Working with ethyl and methyl alcohols, ortho, meta and para substituted benzoic acids they showed that the toluic acids were esterified in the following order: meta, para and ortho. The same held good for other monosubstituted benzoic acids.

Kellas[6] extended the work of Victor Meyer and found practically the same results. He also studied the rate of saponification of esters of the substituted benzoic acids by KOH. In the case of the esters of the toluic acids the results are so close together that no general relation can be gotten from them.

Recently McCombie and Scarborough[7] in studying the rate of saponification of esters of substituted benzoic acids by HCl found the following constants:

	ortho	meta	para
Toluic	0.00134	0.00405	0.00275
Chlorbenzoic	0.0158	0.0485	0.0208
Brombenzoic	0.0118	0.0445	0.0234

Thus we see that the saponification relation is the same as that of esterification.

Reid[8] in studying the mechanism of the reaction in esterification showed that mercaptans esterify acids just as do alcohols. However instead of getting esters of the general formula RCOOR[1] he got the thiol esters of the

4 Petersen, Zeit, fur Phys. Chem. 16, 403 (1895).
5 V. Meyer, Ber. 27, 510; 3146 (1894); Ber. 28, 1254; 2773; 3197 (1895). Zeit. fur Phys. Chem. 24, 219 (1897).
6 Kellas, Zeit fur Phys. Chem. 24, 221 (1897).
7 McCombie and Scarborough, J. Chem. Soc. 107, 156 (1915).
8 Reid, Am. Chem. J. 43, 489 (1910).

general formula $RCOSR^1$. This shows conclusively that esterification takes place as follows:

$$RCO|\overline{OH \quad H}|OR^1 \rightleftarrows RCO|\overline{OR^1 \quad H}|OH$$

$$RCO|\overline{OH \quad H}|SR^1 \rightleftarrows RCO|\overline{SR^1 \quad H}|OH$$

The present work was taken up therefore with the idea of finding whether or not the above relations hold when the toluic acids are esterified with ethyl mercaptan.

MATERIALS.

ACIDS.

The ortho and meta toluic acids were a well known firm's best grade. The para toluic acid was made from para tolyl nitrile which, in turn, was made from para toluidine by the Sandmeyer reaction. This acid was purified by boiling with animal charcoal and then twice recrystalizing from boiling water. M. P. 177°.

MERCAPTAN.

The ethyl mercaptan was made by Reid for use in the above mentioned work. It was freed from sulphide, dried, and twice distilled, only the best fraction being used for the work.

The thiol esters were made by alkylating the thiol toluic acids which were prepared according to the directions of Kym.[9]

ORTHO THIOL TOLUIC ACID.

To 80 grams of 85% KOH dissolved in 600 cc of 95% alcohol and saturated with H_2S, there was added with cooling 70 grams of ortho tolyl chloride. The potassium salt of the ortho thiol acid separated at once as a pasty brown mass. This was dried on the water bath, taken up with water and the solution shaken with ether in order to remove any ethyl toluate that might have been present. On acidifying the water solution of the potassium salt with HCl the acid separated out as a red oil. This was taken up with ether, the ethereal solution dried over $CaCl_2$

9 Kym, Ber. 32, 3533 (1899).

and after distilling off the ether, the ester was twice distilled. The yield was 26 grams. B. P. $133°_{35}$. D.1.1451 $\frac{25}{25}$ Weighed portions of the acid were dissolved in alcohol and titrated with $\frac{n}{.0905}$ $Ba(OH)_2$.

I. .1559 gram acid took 11.32 cc alkali; corresponds to M. W. 152.18.

II. .1418 gram acid took 10.62 cc alkali; corresponds to M. W. 152.71.

Calculated M. W. 152.12.

PARA THIOL TOLUIC ACID.

This was made in exactly the same way as the ortho. The acid separated as a red oil which on cooling, solidified. 48 grams were gotten from 70 grams of para tolyl chloride. B. P. $131°_{15}$. M. P. after recrystallizing from alcohol 43.5-44. This was also titrated with $Ba(OH)_2$.

I. .1409 gram acid took 10.30 cc alkali; corresponds to M. W. 152.64.

II. .1981 gram acid took 14.44 cc alkali; corresponds to M. W. 152.38.

The meta thiol toluic acid and its ethyl ester could not be made on account of the scarcity of meta xylene and meta toluidine.

ETHYL ORTHO THIOL TOLUATE.

This was made by Wheeler's method[10] from potassium ortho thiol toluate and ethyl bromide. 25 grams were gotten from 30 grams of the acid and 35 grams of ethyl bromide. B. P. $133°_{15}$. D. $1.0513\frac{25}{25}$. The ester has a clear yellow color which has remained unchanged after standing five months.

10 Wheeler, Am. Chem. J. 24, 69 (1900).

ETHYL PARA THIOL TOLUATE.

This was made exactly as was the ortho ester. From 25 grams of the acid and 30 grams of ethyl bromide 23 grams of the ester were obtained. B. P. $150°_{18}$. D. $1.0708\frac{25}{25}$. This ester has also remained unchanged on five months standing.

All of these acids and esters are insoluble in water, but dissolved readily in alcohol and ether. They are very resistant to oxidation by nitric acid, for after heating them 5 hours in a Carius tube with concentrated HNO_3 at 250, they were not burned up.

The authors have been working for some time upon a new method for the determination of sulphur in organic compounds. The analysis of these acids and esters will appear in a later paper upon this method.

WATER.

Conductivity water used.

HEATING.

The furnace used was that described by Pratt and Reid;[11] electrically controlled and heated, it maintained the desired temperature for weeks with a variation of $\pm$ 2 C.

STANDARD SOLUTIONS.

The standard HCl and $Ba(OH)_2$ were kept in large stock bottles from which they were run through a siphon, fitted with a stop-cock, into their respective burettes. The top of the HCl bottle and burette was protected from the air by tubes containing HCl of the same strength as that in the stock bottle. The $Ba(OH)_2$ system was protected by soda lime tubes. Both solutions were approximately $\frac{n}{10}$ and were frequently sandardized.

11 Pratt and Reid, J. Am. Chem. Soc. 37, 1934 (1915).

PROCEDURE.

Hard glass tubes about 6 by 70 mm, closed at one end, were cleaned by boiling one day in dilute HCl, 4 hours in distilled water and then thoroughly dried in an air bath at 150°.

ACID SERIES.

Each tube was weighed, partly filled with the toluic acid, drawn out to a narrow neck and weighed again. The mercaptan was then added and after cooling in ice and salt, the tubes were sealed. The tube and tip were then weighed.

ESTER SERIES.

The procedure was the same as for the acid series, using ester instead of acid and water instead of mercaptan.

These tubes were then placed in the furnace and heated to 198-202° for different periods of time. On taking the tubes from the furnace they were allowed to cool, scored with a file and broken into 120 cc Erlenmeyer flasks. 25 cc of ethyl alcohol which had been distilled from KOH were then added, and after dissolving the reaction mixture, the mercaptan which had not reacted, was blown off by bubbling through the solution, kept at 50°, a current of CO_2 free air for 15 minutes. The amount of toluic acid present was then determined by titration with the standard $Ba(OH)_2$ solution using phenolphthalein as an indicator. Uniformity of results was gotten by standardizing the $Ba(OH)_2$ with alcoholic solutions of the toluic acids used.

EXPERIMENTAL.

Two things are of interest, the rates and the limits of esterification of the various acids. The velocities of esterification are calculated by the formula for bimolecular reactions.

$$K = \frac{2.3025}{(A - B)t} \log \frac{(A - x)B}{(B - x)A}$$ [12]

in which A and B are the active masses of the two substances that react, x the amount of each transformed and t the time. As this equation holds only when the reaction is proceeding with an appreciable velocity, it was applied to only the one, two and four day series.

The limits of esterification are gotten by the usual reasoning in consideration of reversible reactions.[13] In this case the amount of ester formed in unit time being equal to (Acid $\times$ Mercaptan) K and the amount of ester decomposed at the same time being equal to (Ester $\times$ Water) K^1, at equilibrium these velocities being equal, we have

$$\frac{\text{(Acid Mercaptan)}}{\text{(Ester Water)}} = \frac{K^1}{K} = r$$

For equal concentrations of acid and mercaptan at equilibrium

$$\frac{\text{Amount of mixture unesterified}}{\text{Amount of mixture esterified}} = \frac{\sqrt{K_1}}{\sqrt{K}} = \frac{\sqrt{r}}{1}$$

or the percentage of a mixture of equivalent amounts, esterified at limit $= \frac{100}{\sqrt{r} + 1}$

12 Reid, Am. Chem. J. 24, 398 (1900).
13 Reid, Am. Chem. J., 43, 499 (1910). Bonz. Z. fur Phy. Chem. 2, 865 (1888).

In the following tables are given the results of the ortho, meta, para toluic acids, ethyl mercaptan series and the results of the ortho, para ethyl ester, water series.

In tabulating the results, the data are thus arranged:

a. Acid or ester in grams.

b. Millimols of acid or ester.

c. Mercaptan or water in grams.

d. Millimols of mercaptan or water.

e. Cubic centimeters of standard alkali required for titration.

f. Millimols of acid present calculated from E.

g. Millimols of mercaptan remaining (acid series).

h. Millimols of ester remaining (ester series).

k. Millimols of water remaining (ester series).

m. Millimols of ester water (acid series).

%. Percentage of esterification, calculated by the above formula.

x. The same as m in acid series and f in ester series.

K. The velocity constant of the reaction.

In the acid series the amount of ester given (m) is found by subtracting the acid remaining (f) from the original amount (b). The concentration of ester (m) equals the concentration of water. The millimols of mercaptan remaining, as given in (g), is gotten by subtracting the amount of ester (m) from (d), the amount of mercaptan originally present.

In the ester series, the amount of ester given (h) is found by subtracting the acid present from (b), the original amount of ester. The water remaining (h) is obtained by subtracting the acid present (f) from (d), the original amount of water.

The percentage esterification (%) and the velocity constant of the reaction (K) are gotten by calculation with the above discussed equations.

RESULTS.

SERIES I.

24 Hours at 200°.

o $CH_3C_6H_4COOH + C_2H_5SH$

a	.0669	.0935	.0817	.0774	.0778	.0910
b	.4919	.6875	.6007	.5691	.5722	.6691
c	.1242	.1206	.1605	.0941	.1680	.1095
d	2.001	1.9428	2.586	1.515	2.707	1.765
e	5.32	7.21	6.48	5.98	6.21	7.09
f	.4816	.6529	5.846	5.412	.5625	6.419
g	1.991	1.9082	2.570	1.487	2.697	1.738
m	.0103	.0346	.0161	.0279	.0097	.0272
r	95.07	32.26	76.13	32.15	127.9	38.83
%	1.04	3.01	1.30	3.02	0.78	2.51
K	.0110	.0267	.0101	.0338	.00637	.0235

Mean K .0186. Mean % 1.94.

m $CH_3C_6H_4COOH + C_2H_5SH$.

a	.1104	.1324	.1412	.1609
b	.8118	.9735	1.0375	1.183
c	.1690	.1705	.1238	.1091
d	2.723	2.747	1.995	1.758
e	8.00	8.72	10.24	11.92
f	.7240	.7882	.9267	1.079
g	2.635	2.5616	1.884	1.654
m	.0878	.1854	.1108	.1040
r	15.73	7.66	11.93	12.85
%	5.98	(11.55)[14]	7.73	7.22
K	.0428	.0697	.0579	.0541

Mean K .0516. Mean % 6.98.

14 Bracketed results not used in calculating averages.

p $CH_3C_6H_4COOH + C_2H_5SH$.

a	.0468	.0420	.0410	.0507	.0479
b	.3441	.3088	.3015	.3728	.3522
c	.2641	.1813	.1621	.1271	.0939
d	4.255	2.921	2.612	2.048	1.513
e	3.48	3.11	3.04	3.85	3.58
f	.3150	.2815	.2751	.3484	.3240
g	4.230	2.894	2.586	2.024	1.485
m	.0291	.0273	.0264	.0244	.0282
r	39.67	33.06	31.95	34.42	24.60
%	2.46	2.94	3.04	2.83	3.91
K	.0207	.0316	.0354	.0331	.0558

Mean K .0353. Mean % 3.03.

o $CH_3C_6H_4COSC_2H_5 + H_2O$.

a	.2846	.2734	.2601	.2820	.2875	.2722
b	1.5807	1.5184	1.4447	1.5662	1.5968	1.5180
c	.2891	.2104	.2003	.1634	.1357	.1398
d	16.061	11.688	11.128	9.078	7.539	7.767
e	2.60	2.70	2.01	1.44	1.92	2.66
f	.2353	.2444	.1819	.1303	.1738	.2407
h	1.3454	1.2740	1.2628	1.4359	1.4230	1.2711
k	15.826	11.446	10.946	8.948	7.365	7.526
r	.0510	.0640	.0489	.0364	.0537	.0778
%	95.18	93.98	95.32	96.50	94.90	(92.80)
K	.0102	.0153	.0125	.0126	.0154	(.0229)

Mean K .0132. Mean % 95.17.

p $CH_3C_6H_4COSC_2H_5 + H_2O$.

a	.2947	.2551	.2487	.2682	.2544	.2663
b	1.6367	1.4168	1.3813	1.4897	1.4129	1.4790
c	.1411	.1747	.1307	.1862	.1594	.1844
d	7.8390	9.7055	7.2610	10.3440	8.8555	10.2440
e	8.55	5.95	3.86	5.95	8.08	8.14
f	.7738	.5385	.3493	.5385	.7312	.7367
h	.8629	.8783	1.0320	.9512	.6817	.7423
k	7.0652	9.1670	6.9117	9.8055	8.1243	9.5073
r	.3134	.1898	.1308	.1763	.3106	.2774
%	76.17	84.05	88.40	85.10	76.30	78.25
K	.0860	.0512	.0409	.0446	.0864	.0712

Mean K .0634. Mean % 81.21.

SERIES II.[15]

48 Hours at 200°.

o $CH_3C_6H_4COOH + C_2H_5SH$.

b	1.0405	1.089	0.9500	0.7522	0.7647
d	3.0285	3.5804	3.9108	1.281	3.2760
f	.9957	1.0300	.8960	.7023	.7321
r	35.91	32.28	34.43	18.66	47.27
%	2.71	3.00	2.83	(5.10)	2.08
K	.00736	.00819	.00742	(.0280)	.00451

Mean K .00687. Mean % 2.65.

m $CH_3C_6H_4COOH + C_2H_5SH$.

b	1.5883	1.0118	1.1831	.9721
d	1.9578	2.3623	2.1544	1.3954
f	1.4426	.8823	1.0208	.8751
r	11.10	10.84	8.79	10.99
%	8.26	8.63	10.23	8.34
K	.0249	.0298	.0343	.0302

Mean K .0298. Mean % 8.81.

p $CH_3C_6H_4COOH + C_2H_5SH$.

b	.4059	.6559	.4956	.5780
d	2.8875	5.2788	2.5507	2.8715
f	.3701	.5819	.4317	.5294
r	28.70	23.51	16.22	25.16
%	3.37	4.08	5.81	3.82
K	.0164	.0114	.0266	.0153

Mean K .0174. Mean % 4.27.

o $CH_3C_6H_4COSC_2H_5 + H_2O$.

b	1.3684	1.5545	1.5507	1.6034	1.6451
d	8.4778	16.061	11.406	12.917	14.067
f	.1376	.2742	.3493	.3321	.2471
r	.0429	.0610	.0958	.0830	.0562
%	95.9	94.2	91.3	92.4	94.7
K	.00627	.00608	.0113	.00890	.00585

Mean K .00768. Mean % 93.7.

15 On account of brevity unnecessary figures are omitted in the following tables.

p $CH_3C_6H_4COSC_2H_5 + H_2O$.

b	1.5579	1.4518	1.4796	1.5723	1.5401
d	15.357	15.723	13.844	16.245	12.111
f	.6598	.9575	1.0605	1.0263	.6552
r	0.182	0.354	0.458	0.356	0.206
%	84.6	73.9	68.6	73.8	83.3
K	.0185	.0357	.0507	.0341	.0233

Mean K .0325. Mean % 76.8.

SERIES III.

96 Hours at 200°.

o $CH_3C_6H_4COOH + C_2H_5SH$.

b	1.2442	1.1589	1.0294	1.2162	.7397
d	2.7746	2.9681	2.1431	3.5562	1.9852
f	1.1421	1.0291	.9068	1.0923	.6667
r	17.13	13.17	11.04	15.63	15.33
%	5.52	7.06	8.32	6.02	6.12
K	.0079	.0102	.0152	.0077	.0125

Mean % 6.61. Mean K .0107.

m $CH_3C_6H_4COOH + C_2H_5SH$.

b	1.6618	1.2455	1.6602	1.4220
d	2.1555	2.6588	2.7925	2.5879
f	1.4281	1.0326	1.4200	1.2064
r	7.10	7.46	7.93	7.85
%	12.35	11.83	11.20	11.30
K	.0196	.0194	.0146	.0166

Mean % 11.67. Mean K .0175.

p $CH_3C_6H_4COOH + C_2H_5SH$.

b	.5721	.6265	.7140	.8029	.9552
d	2.8036	3.1502	2.7022	4.0132	3.8060
f	.4480	.4928	.5883	.3992	.7593
r	8.83	9.54	9.80	3.06	8.45
%	10.18	9.53	9.25	(24.63)	10.58
K	.0223	.0167	.0183	(.0504)	.0155

Mean % 9.88. Mean K .0182.

o $CH_3C_6H_4COSC_2H_5 + H_2O$.

b	1.3612	1.7145	1.5451	1.4917	1.6890
d	3.0667	5.2777	4.7000	4.9890	5.8389
f	.9430	1.0507	.6943	.7521	1.1267
r	1.00	.627	.376	.425	.690
%	50.0	61.4	72.6	70.2	59.2
K	.1180	.0507	.0345	.0383	.0535

Mean % 62.7. Mean K .0590.

p $CH_3C_6H_4COSC_2H_5 + H_2O$.

b	1.3074	1.6140	1.5117	1.5423	1.4168
d	5.6442	6.2833	4.3445	4.5112	3.2834
f	1.2380	1.5159	1.3982	1.4272	1.3104
r	2.24	2.22	2.45	2.40	2.86
%	30.86	31.06	28.98	29.41	25.90
K	.1551	.1348	.1940	.1866	.2779

Mean % 29.24. Mean K .1897.

SERIES IV.

192 Hours at 200°.

o $CH_3C_6H_4COOH + C_2H_5SH$.

b	1.0176	1.2029	1.0537	.9397	.9191
a	1.1893	1.4180	2.0722	1.8208	1.2246
f	.9168	1.0543	.8887	.8018	.8127
r	9.445	7.785	7.891	8.424	8.959
%	9.57	11.38	11.25	10.61	10.04

Mean % 10.57.

m $CH_3C_6H_4COOH + C_2H_5SH$.

b	1.1243	1.3382	1.1676	1.0492	1.2360
d	.7525	1.4760	1.2375	1.6388	1.9062
f	1.0235	1.1655	1.0199	1.8932	1.0524
r	8.102	7.220	7.138	7.307	7.334
%	10.98	12.17	12.29	12.04	12.00

Mean % 11.90.

p $CH_3C_6H_4COOH + C_2H_5SH$.

b	.5647	.5471	.5713	.5875	.5971
d	1.3600	1.5839	1.9915	2.0335	.9877
f	4.606	.4335	.4344	.4543	.5059
r	7.307	7.028	6.560	6.976	7.384
%	12.04	12.45	13.24	12.53	11.93

Mean % 12.43.

o $CH_3C_6H_4COSC_2H_5 + H_2O$.

b	1.3746	1.5518	1.3523	1.2130
d	3.9278	2.5445	3.2222	2.7111
f	1.0715	1.0606	1.1385	.9104
r	1.151	1.242	1.666	1.233
%	46.49	44.60	37.51	44.78

Mean % 43.34.

p $CH_3C_6H_4COSC_2H_5 + H_2O$.

b	1.2757	1.2119	1.2702	1.2930	1.3956
d	4.8833	2.3777	3.3277	2.6777	3.0222
f	1.1982	1.1095	1.1837	1.1873	1.2977
r	2.242	3.080	2.751	2.991	3.158
%	(30.85)	24.52	26.67	25.06	24.05

Mean % 25.07.

SERIES V.

384 Hours at 200°.

o $CH_3C_6H_4COOH + C_2H_5SH$.

b	.7184	.7728	.6897	.5728	.8302	1.0022
d	.7300	.7525	.6832	.6445	.8669	.8782
f	.6176	.6645	.5860	.4932	.7159	.8709
r	6.186	6.041	5.620	5.916	6.424	6.143
%	13.29	14.20	15.11	14.46	13.47	14.00

Mean % 14.19.

m $CH_3C_6H_4COOH + C_2H_5SH$.

b	1.0044	.7772	.7309	.7169	.7103	.8287
d	.6752	.5044	.6494	.6993	.7686	.8057
f	.8926	.6987	.6401	.6212	.6113	.7213
r	6.343	6.950	6.587	6.398	6.588	6.608
%	13.62	12.58	13.18	13.52	13.18	13.14

Mean % 13.20.

p $CH_3C_6H_4COOH + C_2H_5SH$.

b	.6022	.3434	.3794	.5235	.5324	.5662
d	.5898	.7992	.7428	.6188	.2868	.3158
f	.5157	.2750	.3092	.4481	.4806	.5049
r	5.890	6.341	6.496	6.544	6.487	6.561
%	14.51	13.62	13.34	13.26	13.36	13.23

Mean % 13.55.

o $CH_3C_6H_4COSC_2H_5 + H_2O$.

b	1.4745	1.2757	1.4268	1.6301	1,3563	1.4075
d	2.3000	1.8944	2.3945	1.7722	2.2778	1.9722
f	1.2532	1.0683	1.2117	1.3153	1.1657	1.1783
r	2.838	2.581	2.402	3.468	2.532	2.773
%	26.05	27.92	29.40	22.38	28.31	26.50

Mean % 26.42.

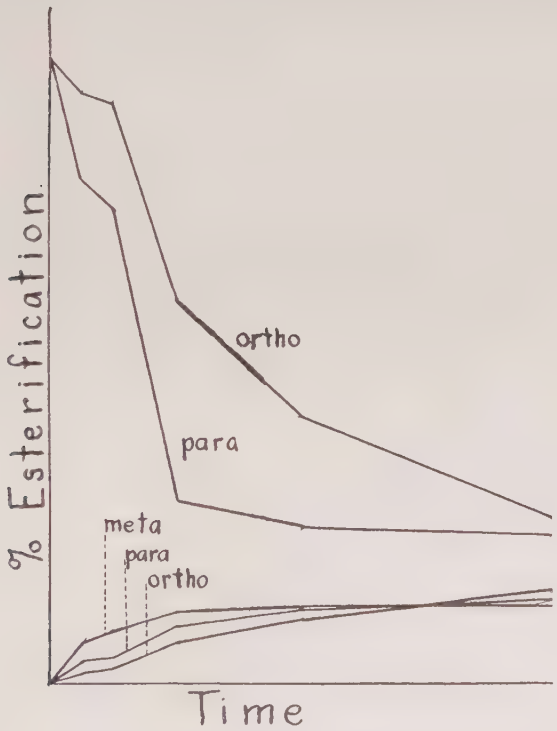
p $CH_3C_6H_4COSC_2H_5 + H_2O$.

b	1.3518	1.4751	1.5912	1.4601	1.5817
d	2.0222	3.6890	4.1222	4.0666	2.9278
f	1.2261	1.3785	1.4857	1.3703	1.4623
r	4.352	2.918	2.820	2.785	3.496
%	18.68	25.52	26.18	26.42	22.24

Mean % 23.81.

SUMMARY OF RESULTS

	Acid Series						Ester Series			
	o		m		p		o		p	
		K		K		K		K		K
1 day	1.94	.0186	6.98	.5016	3.03	.0353	95.17	.0132	81.21	.0634
2 days	2.65	.00687	8.81	.0298	4.27	.0174	93.7	.00768	76.8	.0325
4 days	6.61	.0107	11.67	.0175	9.88	.0182	62.7	.0590	29.24	.1897
8 days	10.57		11.90		12.43		43.34		25.07	
16 days	14.19		13.20		13.55		26.42		23.81	



DISCUSSION OF RESULTS.

On examination of the foregoing results, it is seen that very concordant results are obtained in the acid series, while those from the ester series show large variations. Then, too, the same limit is not reached in the ester series that is gotten in the acid series. The cause of these discrepancies lies, no doubt, in the fact that in the acid, mercaptan series the reaction mixture forms a homogeneous liquid at 200°; in the ester, water series at this temperature the oily ester and the water remain separated in two layers, thus leaving a comparative small surface of contact at which the reaction takes place.

On the whole, the results for the one and two days series are rather unsatisfactory, looking at the curves plotted for the progress of the reaction one sees at once that the reaction seems to lag at two days. As this lag is observed in all five cases it seems probable that the temperature, at which the two day series was run, was low, due, doubtless, to faulty regulation of the furnace. A few degrees at the temperature where these experiments were carried out would make quite a large difference in the short periods of time.

The results for the four, eight and sixteen days series are very good, especially in the acid series, another series was run for the eight day period using larger tubes and smaller amounts of water; furnace trouble developed here and the results proved so unsatisfactory that they are not included. In the ester series there seems to be some relation between the amount of water used and the amount of ester remaining, as a rule, the smaller the amount of water used the more ester was decomposed, which is opposite to what one would naturally expect.

A study of the results of the rates and limits of the esterification of the three acids is very interesting, one is

struck at once by the very large velocity in the case of the meta acid and the small velocity in the case of the ortho acid. The meta acid proceeds over half way to its limit in the first day while the para goes to about 1-4 and the ortho to about 1-7 their respective limits in the same time. Thus these results agree very well with those gotten by the workers cited in the first part of this paper. It seems that the limits in all three cases are about the same (14%), for there is a very small increase in the results of the sixteen day series over those gotten at eight days. In the acid, mercaptan series, especially for the longer times, the amounts of acid and mercaptan have no applicable influence on the limit of the reaction.

In all the experiments run over two days there was a slight amount of decomposition, this was determined by the presence of H_2S which was shown by the lead acetate paper test.

CONCLUSION.

I. Mercaptans esterify acids just as do alcohols.

II. Mercaptans show the same relations between velocities and limits of esterification as do alcohols.

III. The limits in the case of ethyl mercaptan are much lower than in the case of ethyl alcohol.

IV. The limit in the acid, mercaptan series is independent of the amount of reacting substances.

V. Ortho, meta and para toluic acids reach practically the same limit of esterification when esterified with ethyl mercaptan.

BIOGRAPHY.

John Harrison Sachs was born at Gettysburg, Pennsylvania, April 14, 1889. He was graduated from Gettysburg High School in 1905 and from Pennsylvania College, Gettysburg, Pennsylvania, in 1910 with the degree of B.S. After teaching one year in the High School of Dixon, Illinois, and two years in Massanutten Academy, Woodstock, Virginia, he entered Johns Hopkins University in the fall of 1913, where he has pursued graduate studies in chemistry for the past three years. In his first year he held a laboratory assistantship under Dr. Lovelace and for his last year he was awarded a University Scholarship.